

Langmuir Monolayers of 4-methyl-4-mercaptobiphenyl on a Liquid Mercury Surface

H. Kraack (Bar-Ilan U.), B. M. Ocko (BNL), P. S. Pershan (Harvard U.), A. Ulman (Polytech. U. Brooklyn), E. Sloutskin, and M. Deutsch (Bar-Ilan U.)

Beamline(s): X22B

Introduction: Self assembled monolayers (SAMs) of n-alkanethiols on gold have been studied extensively due to their technological relevance and their scientific importance. Following the recent study of the Ångström-scale structure of SAMs of 4-methyl-4-mercaptobiphenyl, $\text{CH}_3\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-SH}$ (MMB) on an Au(111) surface[1], where epitaxy to the crystalline structure of the Au surface was found to play a dominant role, we report here a study of MMB on the surface of mercury, a liquid, unstructured metallic surface. X-ray Reflectivity (XR), Grazing Incidence Diffraction (GID) and Bragg Rod (BR) measurements[2] were carried out at the liquid surface X-ray spectrometer at beamline X22B, to determine the structure of the monolayer, and its variation with the area per molecule.

Results: Fig.1 shows the measured (points) and fitted (lines) XR curves (a) for coverages of 50 (1), 30 (2) and 23 (3) $\text{\AA}^2/\text{molecule}$ along with the electron density profiles derived from the fits (b). Two phases can be distinguished: The low coverage phase (50 $\text{\AA}^2/\text{molecule}$) is consistent with the molecules lying down on the mercury surface, and forming a single layer about 7 Å thick. No in plane order was found for this phase. The high coverage phase (23 $\text{\AA}^2/\text{molecule}$) has an XR-derived thickness of 13.2 Å and exhibits a single GID peak at $q_{\parallel} = 1.381 \text{ \AA}^{-1}$ (Fig.2), corresponding to a hexagonal unit cell with a molecular area of 23.9 $\text{\AA}^2/\text{molecule}$. The BR fit (Fig.2 inset) yields a 12° molecular tilt in the nearest neighbour direction, but with an undistorted hexagonal packing in the surface plane. A coexistence range between the low and high coverage phases was also found at 30 $\text{\AA}^2/\text{molecule}$ (2).

Conclusions: The two systems, MMB on gold and MMB on mercury, show many similarities: For low coverage the MMB molecules lie down on the mercury as well as on the gold surface, with a similar molecular area. While the MMB molecules are commensurate with the gold and form an ordered layer, no in-plane order was found for MMB on mercury. For high coverage the molecules form a tilted hexagonal phase of standing-up molecules in both systems. For MMB on gold the structure is commensurate with that of the Au surface and can be described by a $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ lattice with a molecular area of 21.6 $\text{\AA}^2/\text{molecule}$. For MMB on mercury, however, a much larger molecular area of 23.9 $\text{\AA}^2/\text{molecule}$ is found. A full analysis of our results and a comparison with those of MMB on Au is in progress.

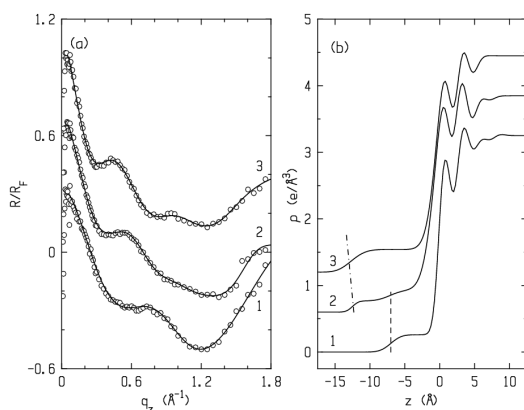
References:[1] T.Y.B. Leung *et al.*, *Surface Science* **458**, 34 (2000)[2] M. Deutsch and B. M. Ocko in *Encyclopedia of Applied Physics*, G. L. Trigg (ed.) (VCH, NY, 1998), Vol. 23, p. 479 ; *X-Ray and Neutron Reflectivity: Principles and Applications* Eds. J. Daillant and A. Gibaud (Springer, Berlin, 1999).

Fig.1: Measured and fitted XR (a) for coverages of 50, 30 and 23 $\text{\AA}^2/\text{molecule}$ of MMB on mercury and their fitted electron density profile (b). Curves 1,2 and 3 correspond to the lying-down, coexistence and standing-up phases, respectively.

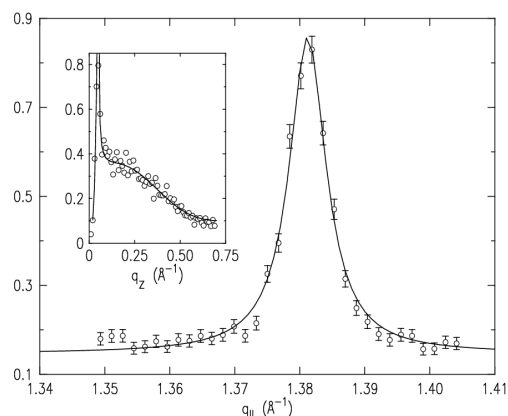


Fig.2: The measured (q_{\parallel}, q_z) diffraction pattern for the high coverage standing-up hexagonal phase of MMB on mercury. The BR scan, shown in the inset, is consistent with the molecules having a 12° tilt in the nearest neighbour azimuthal direction.